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Radiochemical Studies of Chemisorption and Catalysis

XII. Studies of the Adsorption of [^{14}C]Acetylene, [^{14}C]Ethylene and [^{14}C]Carbon Monoxide on Silica- and Alumina-Supported Rhodium Catalysts

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The interaction of ^{14}C-labeled acetylene, ethylene and carbon monoxide with rhodium supported on silica or alumina catalysts has been studied at room temperature at pressures of a few Torr. Adsorptions of acetylene, carbon monoxide and ethylene were performed separately: adsorptions of each of these gases followed by another were also studied. The behavior of the system was observed by counting of surface radioactivity. Acetylene gave adsorption isotherms with two well-defined regions, one of which, the primary region, was steeply sloping. [^{14}C]CO as a probe for metal sites showed that few were left after adsorption of acetylene. CO-precoverage of the metal surface showed that the extent of secondary adsorption of acetylene was unchanged and that this adsorption was probably associated with the support. C_2H_2 had the ability to displace about 40% of the adsorbed CO. This study is to be taken in conjunction with Part XIII of the series, in which mass spectrometry was used to elucidate the nature of the reactions occurring.

INTRODUCTION

In previous papers in this series (*1–3*) we have reported on the behavior of ^{14}C-labeled molecules when they interacted with supported noble-metal catalysts. [^{14}C] ethylene, on Rh/silica and Rh/alumina, underwent adsorption at room temperature on to the metal and migrated to the support (*4*). Mass-spectrometric study of this interaction revealed self hydrogenation as the principal reaction occurring on the metal (*5*).

In this study, we have been interested in the adsorption of [^{14}C]acetylene on rhodium on silica and rhodium on alumina catalysts, and in its behavior when compared with [^{14}C]carbon monoxide and [^{14}C]ethylene, the former in the role of detector of metal sites.

EXPERIMENTAL

The 5% Rh/silica catalyst was from the same stock as that used previously (*4*). Fifteen percent Rh/silica was prepared by an analogous method and 5% Rh/alumina was prepared by impregnating a slurry of γ-alumina (Degussa Ltd.) with an aqueous solution of $RhCl_3$, evaporating to dryness, followed by reduction at 200°C for 24 hr in a stream of hydrogen.

Acetylene (British Oxygen Co. Ltd.) was purified by fractional distillation. [^{14}C] Acetylene (Radiochemical Centre, Amersham) was diluted to a specific activity of 0.1 mCi/mmole with inactive acetylene. This was the specific activity of the [^{14}C] carbon monoxide and [^{14}C]ethylene used previously (*4*). A gas-phase count rate of 500 counts min^{-1} corresponded to a pressure of radioactive gas of 7.5×10^{-2} Torr.

The procedure for studying adsorption and for the cleaning and reactivation of

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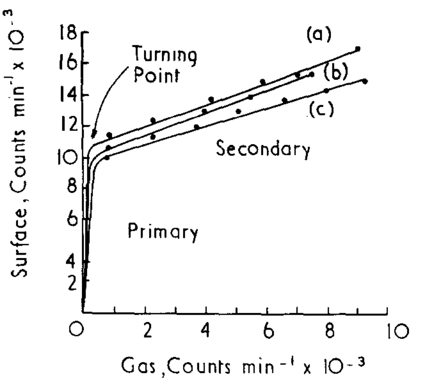

FIG. 1. Adsorptions of $^{14}C_2H_2$ on 5% Rh/SiO$_2$. (a), (b), and (c) represent repeated adsorptions on the same catalyst.

catalysts was the same as that described earlier (4).

RESULTS

All adsorptions were made at room temperature, about 18°C.

Separate Adsorptions, Acetylene and Ethylene

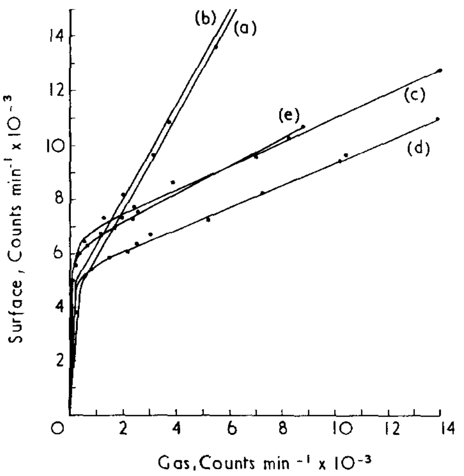

FIG. 2. Separate adsorptions of $^{14}C_2H_2$ and $^{14}C_2H_4$ on the same 5% Rh/SiO$_2$. (a) and (b), $^{14}C_2H_2$; (c), (d), and (e), $^{14}C_2H_2$.

TABLE 1

$[^{14}C]$ACETYLENE ADSORPTION ON Rh/SiO$_2$, Rh/Al$_2$O$_3$, Al$_2$O$_3$ AND SiO$_2$

Absorbent	Counts min^{-1} at turning point	Secondary gradient	Evacuation for 1 hr, counts min^{-1} Before	After
5% Rh/SiO$_2$	6500	0.4	16303	8850
(different	4000	0.4	11211	5281
samples)	5000	0.4	10836	6820
	4500	0.6	—	—
	6250	0.5	—	—
	5000	—	6761	5850
15% Rh/SiO$_2$	16000	0.5	—	—
5% Rh/Al$_2$O$_3$	7500	0.65	—	—
SiO$_2$	None	0.1	2279	650
Al$_2$O$_3$	None	~0.24	6144	1684

Adsorptions isotherms with typical shapes for $[^{14}C]$acetylene on 5% Rh/silica are shown in Fig. 1. Comparative adsorptions for $[^{14}C]$ethylene and $[^{14}C]$ acetylene are shown in Fig. 2, again on 5% Rh/SiO$_2$. The graphs show regions where there is a pronounced change of gradient: for brevity we shall refer to this as the turning point. Acetylene adsorptions on 5% Rh/SiO$_2$, 15% Rh/SiO$_2$, 5% Rh/Al$_2$O$_3$, SiO$_2$ and Al$_2$O$_3$ are shown in Table 1. The effect of a prolonged time of contact is shown in Table 2. Adsorption on alumina is shown on Fig. 3.

For the experiment reported in Table 2, $[^{14}C]$acetylene was admitted to the 5% Rh/SiO$_2$ catalyst in batches and then the system was evacuated. The same amount of gas-phase acetylene as had been finally present was then readmitted and the system left for 16 hr.

Effect of Carbon Monoxide on Acetylene Adsorption

The 5% Rh/SiO$_2$ catalyst was exposed to carbon monoxide at a pressure of a few Torr and the system was evacuated for 1 hr. $[^{14}C]$Acetylene was admitted in

TABLE 2

EFFECT OF LONG TIME OF EXPOSURE OF $[^{14}C]$ACETYLENE TO 5% Rh/SiO$_2$

Surface count rate, counts min^{-1} (before)	Operation and time lapsed	Surface count rate, counts min^{-1} (after)
9842	Evacuation 1 hr	5700
5700	Admission $^{14}C_2H_2$	10112
10112	Lapse of 16 hr	11298
11298	Evacuation 1 hr	8000

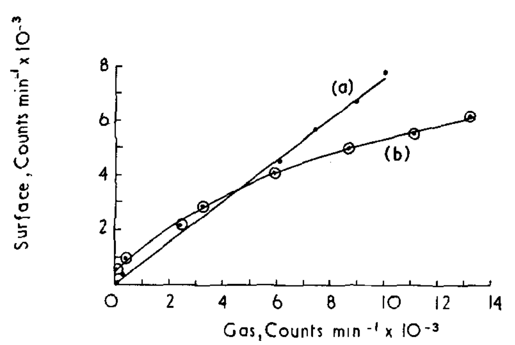

FIG. 3. Separate adsorptions of (a), $^{14}C_2H_4$ and (b), $^{14}C_2H_2$ on alumina.

batches. Figure 4 shows the adsorptions observed.

Displacement Studies

Quantitative displacement studies (*4*), using ^{14}C-labeled species, were made as follows. Adsorptions were allowed to take place to an extent well past the turning points seen in the adsorption graphs, or well into the plateau region in the case of carbon monoxide: a typical turning point is shown in Fig. 1. The systems investigated, where either the surface species or the gas species were ^{14}C-labeled, were the following:

Precoverage of surface by:	Displacement by:
CO	C_2H_2
C_2H_2	CO
C_2H_2	C_2H_4
C_2H_4	C_2H_2

The results are shown in Table 3 and in Fig. 5a and b.

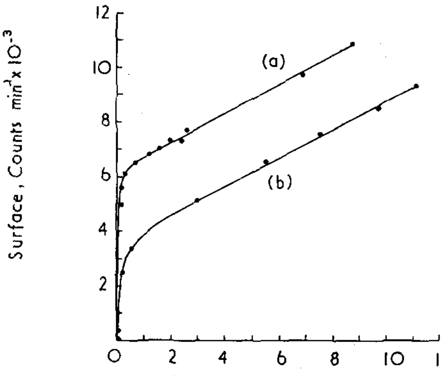

FIG. 4. Adsorption of $^{14}C_2H_2$ on (a), a "clean" 5% Rh/SiO_2 catalyst, and (b), the same catalyst preexposed to CO.

[^{14}C]CO Probe for Bare Metal Sites after [^{14}C]Acetylene Adsorption

As in the experiments involving adsorbed ethylene (4), it was necessary to assess whether bare metal sites remained on rhodium after adsorptions of acetylene. Two experiments were conducted, as shown in Table 4.

Effect of Hydrogen on Surface Species from Adsorbed Acetylene

After a short evacuation for removal of the gas phase after adsorption of $^{14}C_2H_2$, hydrogen, 25–30 Torr, was admitted at room temperature. The surface count rate behavior is shown in Fig. 6. The effect of hydrogen on species from acetylene adsorbed on a carbon monoxide precovered surface is also shown in Fig. 6.

TABLE 3

DISPLACEMENT STUDIES ON 5% Rh/SiO_2

Adsorbate	Measured turning point, counts min^{-1}	Surface, counts min^{-1}	Displacing gas	Pressure Torr	Surface, counts min^{-1}	Percent removal
[^{14}C]CO	12500	12181	C_2H_2	2.5	7415	39.1
	8000	8830			5470	38.1
[^{14}C]C_2H_2	4000	5954	CO	2.5	5869	1.4
	3250	7696		7.5	7400	3.8
[^{14}C]C_2H_4	2250	6584	C_2H_2	45	5955	9.5
[^{14}C]C_2H_2	4750	10160	C_2H_4	45	9000	11.4

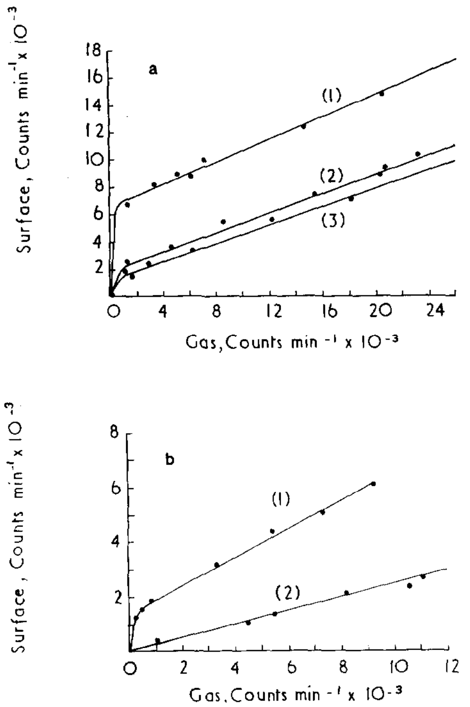

FIG. 5a. $^{14}C_2H_2$ adsorptions on same sample of 5% Rh/SiO_2. (1) Clean catalyst: (2) and (3), catalysts pre-covered by C_2H_4. (b), $^{14}C_2H_4$ adsorption on (1), a clean 5% Rh/SiO_2 catalyst: (2), on the same catalyst precovered by C_2H_2.

The investigation also examined removal of species from acetylene adsorbed in the primary and secondary regions of adsorption: adsorptions were made into the primary region only, and then into primary and secondary regions before hydrogen admission. The results are shown in Table 5.

We examined the "exchange" reactions which occurred when surfaces were covered by [^{14}C]C_2H_2 or [^{14}C]C_2H_4 and inactive samples of C_2H_2 or C_2H_4 were admitted under the conditions set out in the Table 6.

TABLE 4

[^{14}C]CO PROBE FOR METAL SITES AFTER ADSORPTION OF [^{14}C]C_2H_2 ON 5% Rh/SiO_2

Initial [^{14}C]C_2H_2 adsorption, counts min^{-1}	Counts min^{-1} after evacuation	[^{14}C]CO uptake counts min^{-1}	[^{14}C]C Monolayer, counts min^{-1}
15303	7857	300	16500
9807	5820	Zero	13500

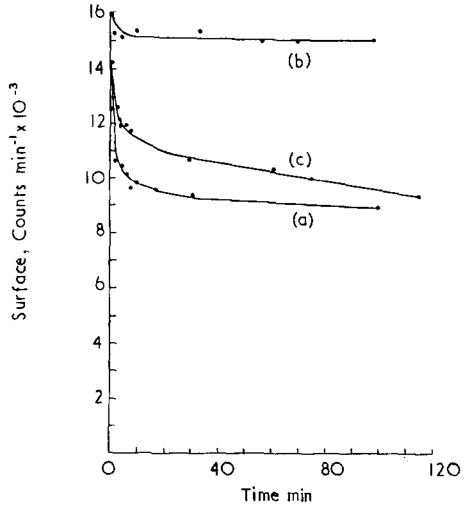

FIG. 6. Removal by hydrogen of species from 5% Rh/SiO_2 on which had been adsorbed, (a), $^{14}C_2H_2$, (b), CO followed by $^{14}C_2H_2$, (c), shows removal by (1:1) C_2H_2/H_2 from a $^{14}C_2H_2$ precovered surface.

DISCUSSION

The results reported in this paper arise from an ability to examine the adsorption behavior of two species, when one of them is labeled by carbon-14: as will be seen later (Part XIII), adsorption was accompanied by self hydrogenation. The results obtained are compatible with the ideas expressed (*4*) for ethylene adsorption under similar conditions. We proposed for ethylene that primary adsorption occurred on the metal and that secondary adsorbed species arose by migration of adsorbed species from metal to support. This proposal applies equally well to the interpretation of the results for acetylene adsorption.

As in the case of [^{14}C]ethylene adsorption (*4*), two distinct regions existed for adsorption of [^{14}C]acetylene (Figs. 1 and 4). Gradients for primary adsorption were steeper, and amounts adsorbed up to the turning point were higher, than for ethylene. This may be the result of higher heats of adsorption for acetylene on metals (*6*).

Secondary gradients for acetylene were

TABLE 5
REMOVAL OF SPECIES FROM [^{14}C]C_2H_2 ADSORPTION ON 15% Rh/SiO_2 AND 5% Rh/Al_2O_3 BY HYDROGEN

Adsorbent	Adsorption type	Counts min^{-1} at turning point	Final counts min^{-1}	Amounts removed by H_2 in counts min^{-1}
15% Rh/SiO_2	primary		16940	12000
	primary + secondary	16500	21900	12500
5% Rh/Al_2O_3	primary	—	4757	2000
	primary + secondary	5000	6607	2100

less steep than those found for ethylene. Change of metal loading from 5 to 15% did not affect the secondary gradient, whereas change of support from silica to alumina did affect significantly the gradient observed for secondary adsorption. For this, and other reasons, we assign secondary adsorptions to the support.

Evacuation for an hour removed more surface species after acetylene adsorption than after ethylene adsorption (Table 1). Few metal sites were left bare after evacuation, as determined by ^{14}CO uptake. When the amount of secondary adsorption was small, (example 6, Table 1), very little was removed by evacuation. Thus we conclude that evacuation removes only secondary material.

If secondary material were associated with the support, then precoverage of the metal on the catalysts by carbon monoxide should have left secondary gradients unchanged when comparison is made with clean catalysts. Figure 4 shows that the primary region was reduced rather than absent, for C_2H_2 could displace CO (Table 3a). Secondary gradients were unaltered as can be seen in Fig. 5.

When ^{14}CO was used as a probe for bare metal sites after Rh/SiO_2 had been exposed to acetylene, it was found that these did not exist (Table 4). This observation is in accord with the more extensive adsorption of acetylene as compared with ethylene (*4*): in the latter case, some bare sites existed at the turning point in the adsorption curve. These differences are also exemplified in Fig. 5a and 5b: acetylene precoverage left no bare metal sites in Fig. 5b.

Hydrogen had a significant effect in the removal of species from the Rh/SiO_2 catalysts exposed to acetylene. The results in Table 5 were consistent with removal of species from metal and support. It is surprising that constant amounts were removed in the circumstances reported in Table 5. The extent to which species were removed corresponded to 12,000 and 12,500 counts min^{-1} for 15% Rh/SiO_2 and for 5% Rh/Al_2O_3, respectively.

The behavior of carbon monoxide in displacing adsorbed species from ethylene

TABLE 6
"EXCHANGE" STUDIES ON 5% Rh/SiO_2

Adsorbate	Turning point, counts min^{-1}	Final surface, count rate rate min^{-1}	Displacing gas	Pressure, Torr	Surface, counts min^{-1}	Percent removal
$^{14}C_2H_4$	5500	10997	C_2H_4	25	10300	6.3
$^{14}C_2H_4$	2500	7148	C_2H_4	45	6422	10.2
$^{14}C_2H_2$	3500	5281	C_2H_2	45	4950	6.3
$^{14}C_2H_2$	3750	9655	C_2H_2	45	7500	22.3

(*4*) and acetylene can now be compared. Ethylene displaces very little adsorbed carbon monoxide and the expectation that carbon monoxide might displace some ethylene was fulfilled. On the other hand, acetylene could readily displace carbon monoxide (Table 3) whereas the opposite was not the case.

On this basis, we might have expected acetylene to displace species derived from ethylene adsorption; ethylene would not be expected to displace acetylene. These expectations were not fulfilled, for in Table 3 it is seen that about 10% of surface species were removed in displacements of acetylene by ethylene and ethylene by acetylene. Thus it seems that ethylene and acetylene produced a common adsorbed species which could, by exchange or displacement, result in loss of surface counts (Table 6).

In displacement of carbon monoxide by acetylene, it can be seen from the turning points in the adsorption isotherms recorded in Table 3 that acetylene was able to displace carbon monoxide from the metal.

One of the obvious fates for the "secondary" species adsorbed on Rh/SiO_2 and Rh/Al_2O_3 was that they polymerized, either on a few sites on the metal, or on the support. The fact that secondary species were easily removed by evacuation suggests to us that polymerization was unlikely: this was confirmed in thermal and mass-spectrometric analysis (*8*). In addition, if polymeric material was readily formed as gas pressure increased, we might have expected steeper secondary gradients for acetylene than the less-easily polymerized ethylene (*7*).

The enhanced primary uptake of acetylene compared with ethylene might be due to the formation of C_4, C_6, and other polymeric species. The slow uptake from the gas phase of additional acetylene may be explained on this basis: they would not have been removed by evacuation.

When the results of Table 2 are examined, it is apparent that, on long standing, the amount of ^{14}C species retained on evacuation increased, and the amount retained exceeded that taken up in the slow sorption: some of the acetylene taken up in the initial primary and secondary stages was now bound to the surface, perhaps as polymeric material.

It may be concluded that the adsorption of acetylene on silica- and alumina-supported rhodium catalysts is characterized by two distinct types of adsorbed species; namely, those which give rise to primary adsorption and which were probably associated with the metal, and species which give rise to secondary adsorption, which we believe to be associated with the support. On the basis of the results in this paper it is not possible to deduce the nature of these adsorbed species, or the nature of the surface reactions which occurred in these systems. Such information has been obtained using a thermal desorption technique, the results from which will be reported in a subsequent paper (Part XIII), together with a further appraisal of the results presented in this paper.

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